CONVERSION OF VACUUM PYROLYTIC OILS FROM POPULUS DELTOIDES OVER H-ZSM-5

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INTRODUCTION

As biomaterials are structurally and chemically complex, biomass thermochemical conversion processes[1,2] produce complex fractions including a liquid fraction which, depending on the process, can be obtained in large (liquefaction, pyrolysis) or small yields (gasification). These liquids have found little utility because of their large contents in oxygen which implies low heat values, instability and corrosive properties. Two routes have been tested[3,4] in order to produce hydrocarbons from these liquids. The first one involves hydrotreatment with either H_2 or H_2 + CO over classical hydrotreatment catalysts. The second route is the simultaneous dehydration and decarboxylation over HZSM-5 zeolite catalyst in the absence of any reducing gas.

Soltes and Lin[5] achieved significant deoxygenation of various biomass tars from gasification/pyrolysis processes, in the presence of hydrogen-donor solvents (cyclohexane, tetralin, decalin) and various silica-alumina supported metals catalysts. Elliot and Baker[6] performed hydrodeoxygenation of the products of a process of liquefaction in the presence of CO at high pressure, using NiS, CoS and MoS_2 catalysts. Hydrodeoxygenation of a biomass tar can be achieved when phenolic compounds are in high concentrations. In wood pyrolysis however, the liquid products contain large amounts of low molecular weight organic acids, ketones, aldehydes and furans as well as phenolic compounds in the methoxy- or dimethoxy[6-8] substituted forms. These mixtures are thermally instable in typical hydrotreating conditions.

The second route however seems more appropriate for the conversion of pyrolytic oils. It was indeed shown that a large variety of oxygenated compounds can be converted into hydrocarbons over H-ZSM-5[9-20]. In all cases hydrocarbons in the gasoline range are obtained due to the shape selective properties of this zeolite catalyst[21]. Moreover a remarkable resistance to coking is observed due to the sterically restricted transition state selectivity effects, and these properties are also of considerable interest in the context of pyrolytic oils upgrading. Works along this line have been performed by Chantal et al.[22,25] working with oils derived from Aspen Poplar by dense gas extraction, Frankiewicz[23] who used a dual process combining pyrolysis of solid wastes with a catalytic converter and Mathews et al[24] who treated small fractions of the oils produced from wood by their thermochemical process.

In the present paper we report a study of the conversion over H-ZSM-5 catalysts, of the fractionated oil produced by vacuum pyrolysis of Populus Deltoides wood in a process demonstration unit(26).

EXPERIMENTAL

Pyrolytic oil

The oil under study was produced by the vacuum pyrolysis process, currently under development at LAVAL University and CRIQ[26]. The PDU is a six-hearth furnace, 2m high and 0.7 m in diameter. In this unit, the organic vapours and gaseous products are rapidly removed from the reactor through a series of outlet manifolds. Then the vapours are condensed in a primary cooling unit, and recovered as a liquid fraction for each hearth. As shown in Figure 1 four additional liquid fractions are collected in the secondary cooling unit. In this work only the fractions from the primary cooling unit have been studied and designated as oils #1 to #6 corresponding to the six hearthes from top to bottom.

In standard pyrolysis experiments using Populus Deltoides chips, the pressure in the reactor was lower than 80 Torr and the hearth temperatures were 215, 275, 325, 370, 415 and 465°C from top to bottom respectively. Table 1 gives some analytical results for these six oils. The low water contents are due to the separation effect of the primary cooling unit. Formic and acetic acids are considered the most abundant single organic compounds in these oils.

Conversion Reactor

The experimental set-up is a slightly modified version of a reactor described previously[22]. As heating the pyrolytic oils to the reaction temperature is believed to induce thermal polymerisation/condensation reactions, a device was designed in order to preheat the vaporized feed and condense at an appropriate temperature the heavier products. This device is described in Figure 2. Using a syringe pump (SAGE 220) the liquid oil is injected in a controlled flow of helium ($\approx$ 6.0 SCC/min) and first fed to an empty pyrex tube maintained at the same temperature than the tubular reactor. At the outlet of this tube the gas passes through a hot trap (150°C) where a heavy fraction is condensed. The gas flow then enters the microcatalytic pyrex tubular reactor and it is led to the heated (200°C) automatic sampling valve of a Gas Chromatograph (Perkin Elmer, Sigma 115) through a heated line (160°C). After the valve the products are collected as three fractions in three successive traps maintained at 4, -76 and -196°C respectively.

After a test the tubular reactors can be transported to another set-up where they can be regenerated in a controlled flow of dry air at 500°C. The CO_2 and H_2O produced are adsorbed over ascarite and drierite respectively and weighed. The sum of the masses of carbon in CO_2 and hydrogen in H_2O was determined and compared to the measured mass of the coke deposited in each of the two pyrex tubes.

Each experiment was performed using 1.0 $\pm$ 0.2 g of one of the three catalysts designated as H-22, H120 and H-450 undiluted. These are the H forms of ZSM-5 samples prepared by the procedure described as method B' by GABELICA et al[28]. They have Si/Al ratios of 22, 119 and 452, and sodium contents less than 220 ppm as determined by PIXGE[29].

The GC on line with the reactor was equipped with TC and FID detectors and a Porapak-Q column (6 ft, 1/8" OD, 80-100 mesh). In intances were peak identification was in doubt, the fraction in the 4°C trap was further analyzed using another GC (Perkin Elmer Sigma 3) equipped with a FID detector and a capillary column DB-1 (30 m).

In typical runs, oil was injected for about 3 000 s but chromatographic analysis was started at 2 000 s for all experiments.

Experimental design

A statistical experimental design was employed to study the effect of the process parameters, namely, temperature (350-450°C), space velocity CLHSV = 0.5-2.5 h^{-1}) and oil fraction, on various response variables. In order to reduce the number of experiments, a Box-Behnken experimental design[30] was selected. This design is visualized as a cube in Figure 3. Since 6 oil fractions were studied two Box-Behnken cubes were used in order to minimize the number of experiments by studying three oils at a time. Eventhough a discrete variable is employed to represent the oil, in reality the hearth number (1 to 6) follows the reaction temperature on the hearth which is continuous. The experiments were performed in a random manner.

RESULTS AND DISCUSSION

Table 2 shows the experimental results and conditions for the catalytic upgrading tests of the six pyrolytic oils. It gives the weight percents of the various fractions of products collected. Coke #1 corresponds for example to the total weight of the material deposited on the wall of the empty pyrex tube whereas coke #2 is the one left in the tubular reactor (on the catalyst) at the end of a test. The tar collected in the hot trap is designated as the residuum, whereas the cumulative mass recovered in all three cold traps is indicated as "traps".

The composition of the "traps" fraction is the one of the stream leaving the reactor. It is given in Table 2 in a condensed manner as weight percents of various components including C_5-C_{10} hydrocarbons, C_{10}^+ hydrocarbons and oxygenates. These oxygenates are mostly comprising phenolic and furanic compounds. Figure 4 shows some of the characteristics of the six pyrolytic oils. The average molecular weight varies in a continuous manner with the hearth number, showing a maximum value for the oil produced on the 3rd hearth and a minimum value for the one from hearth No 6.

It must be noted that the sum of weight fractions of acetic and formic acids is following a similar pattern except for the oil No 5 which contains much formic acid and is therefore much more acidic. The low content in formic acid of oil No 6 is a clear indication that the solid residue leaving hearth No 5 is very different in nature from the one from hearth No 4 bearing much less intact or slightly degraded cellulose (the main source of formic acid) and much more recondensed material. Figure 5 shows for each oil the average values of the weight percents of coke #1, residuum and the yield in C_5-C_{10} hydrocarbons. It is interesting to note that at least for the first four oils these values are obviously correlated with both oil average molecular weight and acidity (Figure 4). As expected, coke #1 is higher when the oil is heavier, but the residuum is much smaller. This last result can only be understood if the residuum is seen as an intermediate product of gas phase depolymerization which would be faster for the most acidic mixtures. Indeed for example the low residuum value obtained with oil No 5 would then be the result of this oil being much more acidic than the others.

The C_5-C_{10} yield is also correlated with $\overline{M_w}$ (up to oil No 5) but this correlation is the result of a more intricate interaction of various factors. C_5-C_{10} yield does not depend only on molecular size or acidity of the oil but also on its chemical nature. Oil No 3 which contains more lignin fragments in liable to yield small phenolics which are volatile enough to reach the catalyts but which are not converted to hydrocarbons. Similarily oil No 6 which is believed to contain less polysaccharides pyrolysis products shows a very low C_5-C_{10} yield.

The effect of the various parameters on the "traps" weight percent is reported in Figure 6. This term represents roughly the fraction of the oil reaching the catalyst and must therefore be considered as a yield for the preliminary thermal processing. The curves are drawn not taking into account the results for oil No 5. Comparing the curves obtained at 350 and 450°C (both at 1.2 LHSV) shows that increasing the temperature increases the depolymerisation of the oils components. The two curves at 400°C and 0.5 and 2.5 LHSV show that increasing the residence time in the empty tube and the hot trap increases also the depolymerisation yield.

These results show the interest of the experimental procedure adopted in this work as this gas phase thermal depolymerisation which happens at the same temperature than the catalytic process can be studied separately. This is not the case when the vaporized oil is directly injected onto the catalyst and both processes happen simultaneously.

Figure 7 gives the yield in C_5-C_{10} obtained for the various oils as a function of temperature and LHSV. Comparing the curves at 350 and 450°C shows that a rise in temperature increases this yield in proportions roughly similar to the increase of the "traps" fraction (see Figure 6). This suggests that the most important effect of temperature is to increase the yield of thermal depolymerization. This is confirmed by the fact that the oil No 5 which is the most acidic and is more thorougly depolymerized (yielding a higher "traps" fraction) is also showing the highest C_5-C_{10} yield. Similar observations can be made for the effect of contact time at 400°C.

It is interesting to note that for several oils (No 1, 2, 4 and 5) yields close to 30% have been reached. This is to be compared with the results of Chantal et al[22] who obtained maximum yields of 15-17% from SCE oils converted on ZSM-5 in a one step process. Figure 8 shows the variations of the percents of oxygenates in the traps. In line with previous discussion, maximum oxygenates are obtained from oils No 3 and 6 which contain respectively more lignin fragments and more product of high temperature decomposition of recondensed material and which therefore both contain more phenolic compounds.

Time on stream data

Figure 9 reports the results of a set of experiments (not shown in Table 2) designed to assess the deactivation behaviour of the catalyst. In these experiments the feed was a mixture of the six oils. It was injected for a fixed time in the reactor assembly maintained at 400°C. Then the gases leaving the reactor were analyzed and the injection of oil was stopped until the chromatographic analysis was completed, at which time the injection was restarted for another fixed time and this operation was repeated three times.

Figure 9 shows that the composition of the product changes with time on stream, with deactivation appearing after 250-500 s. The decrease in deoxygenation activity is seen from the decrease in H_2O, CO, CO_2 and the increase in oxygenates. The appearance of C_{10}^+ aromatics in the products is of special interest. Since such large compounds cannot be generated within the pores of the ZSM-5 zeolite[21], they can only be generated either on the external acid sites or from the coke deposit as postulated recently[13]. This would also explain the evolution of the C_6-C_{10} aromatics distribution with time on stream, showing a relative increase in C_{10} as well as C_{10}^+.

The time scale for catalyst deactivation is showing the great resistance of the ZSM-5 catalyst to coking. At similar temperatures for example a pellet of H-Y cracking catalyst is deactivated within 2-3 seconds in the FCC process.

CONCLUSIONS

The experimental set-up used in this work allowed to decouple the gas phase thermal conversion of the pyrolytic oils from the catalytic upgrading. These two sets of reactions happen in the same temperature range and are therefore simultaneous when the oil is directly fed to the catalyst. Preliminary thermal conversions include some coking and an important thermal depolymerization. Both reactions are accelerated in the presence of volatile acids in the gas phase. Moreover performing both reactions in a preheater is beneficial to the catalytic conversion first because the deactivation of the catalyst is less important and secondly because depolymerized fragments yield higher conversions to hydrocarbons. C_5-C_{10} hydrocarbon yields as high as 30 wt% have been consistently obtained for reaction times of 2000 s.

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TABLE 1 Some Characteristics of the Pyrolytic Oils

OIL #	% WATER*	FORMIC ACID WT %	ACETIC ACID WT %	$\bar{M}_w$** Mean-Molecular Weight
1	7.8	2.64	3.63	342
2	5.4	2.34	4.13	528
3	4.4	3.73	5.18	572
4	3.9	4.40	3.26	393
5	7.0	7.25	3.16	233
6	3.8	2.60	2.26	123

* determined by Karl-Fisher
** determined by GPC

TABLE 2 Experimental Conditions and Results of Catalytic Upgrading of Pyrolytic Oils.

OIL #	TEMP. °C	LHSV h^{-1}	COKE wt % #1	COKE wt % #2	RESIDUUM wt %	TRAPS wt %	PRODUCT DISTRIBUTION, wt % CO	CO_2	H_2O	C_1-C_4	C_5-C_{10}	OXYG.	BTX	C_{10}^{+}	YIELD C_5 - C_{10}
1	350	1.2	15.2	2.3	50.8	31.6	1.2	1.7	5.6	1.2	61.9	26.0	23.5	3.3	19.3
1	400	0.5	21.7	6.5	10.9	60.9	0.7	0.8	3.7	2.2	48.7	25.7	21.1	18.4	29.7
1	400	2.5	17.4	2.8	54.8	24.9	1.0	2.0	6.2	4.3	57.6	23.9	19.7	4.9	14.3
1	450	1.2	18.7	2.3	40.9	38.1	0.9	1.1	3.2	1.4	76.8	12.0	18.0	4.6	29.3
2	350	0.5	10.0	4.3	62.9	22.9	0.9	1.2	4.5	1.8	52.2	33.7	18.8	5.4	12.0
2	350	2.5	30.5	3.9	31.2	34.4	1.3	2.7	5.5	1.4	51.4	29.5	13.1	8.1	17.7
2	400	1.2	20.6	5.9	26.5	47.1	0.8	1.0	3.4	2.0	45.8	32.5	17.2	14.6	21.6
2	400	1.2	22.9	5.1	28.8	43.2	0.9	1.2	3.8	2.5	44.4	34.1	18.8	13.1	19.2
2	400	1.2	21.3	5.6	24.0	49.1	1.0	1.2	3.1	1.3	45.4	29.9	17.4	17.1	22.3
2	450	0.5	30.9	3.6	9.1	56.4	0.8	1.2	3.1	2.0	48.3	36.3	18.4	8.5	27.2
2	450	2.5	36.6	2.8	22.5	38.0	2.6	4.6	7.2	4.6	54.7	23.3	22.0	2.8	20.8
3	350	1.2	33.1	4.3	30.7	31.9	0.6	0.7	3.2	0.6	47.0	34.0	10.7	13.9	15.0
3	400	0.5	25.4	3.4	25.4	45.8	1.3	1.9	4.5	4.0	42.6	34.6	28.1	11.1	19.5
3	400	2.5	19.2	3.1	46.9	30.8	0.6	0.9	2.4	1.1	34.9	48.8	8.8	11.3	10.7
3	450	1.2	22.3	5.9	29.4	42.3	0.8	0.9	2.3	1.8	88.6	39.0	17.8	16.5	16.3

TABLE 2 Continued ...

OIL #	TEMP °C	LHSV h^{-1}	COKE wt % #1	COKE wt % #2	RESIDUUM wt %	TRAPS wt %	PRODUCT DISTRIBUTION, wt % CO	CO_2	H_2O	C_1-C_4	C_5-C_{10}	OXYG.	BTX	C^+_{10}	YIELD C_5 - C_{10}
4	350	1.2	20.1	2.4	52.4	25.0	1.3	1.7	5.1	1.1	58.1	24.6	22.4	8.2	14.5
4	400	0.5	23.0	2.7	32.4	41.9	1.7	2.2	6.5	2.2	52.6	25.1	27.7	9.8	22.0
4	400	2.5	11.7	2.6	58.3	27.4	1.3	1.8	8.4	1.9	51.3	27.6	20.0	9.7	14.1
4	450	1.2	26.3	3.5	17.5	52.6	0.9	1.3	7.1	4.2	48.0	21.9	16.7	16.5	25.2
5	350	0.5	27.1	3.4	16.9	52.4	1.6	1.9	6.7	1.3	52.2	29.7	26.0	6.6	27.4
5	350	2.5	21.4	8.6	28.6	41.4	0.9	0.6	8.0	1.5	54.3	31.1	22.1	3.5	22.5
5	400	1.2	25.5	3.9	24.5	46.1	0.4	0.5	2.9	1.1	53.1	28.5	19.0	13.6	24.5
5	400	1.2	22.1	4.1	27.9	45.9	0.6	0.9	2.1	1.2	47.9	34.3	17.2	13.0	22.0
5	400	1.2	29.6	3.2	20.3	46.9	0.3	0.5	4.0	1.4	56.9	24.9	20.4	12.0	26.7
5	450	0.5	30.6	5.6	9.7	54.2	0.7	0.9	2.3	3.3	52.9	36.8	22.0	2.6	28.7
5	450	2.5	31.8	1.3	25.2	41.7	2.5	4.7	8.8	12.1	37.1	30.5	30.6	4.1	15.5
6	350	1.2	18.7	2.9	56.7	21.6	0.2	0.3	1.7	0.2	25.1	71.0	6.9	1.5	5.4
6	400	0.5	30.3	12.1	3.0	54.5	0.3	0.3	1.0	0.9	30.7	47.2	11.2	19.9	16.7
6	400	2.5	10.7	2.1	68.2	19.0	1.4	1.9	7.4	2.5	30.7	21.5	19.3	11.7	10.2
6	450	1.2	20.4	2.4	47.9	29.3	1.3	1.2	3.9	5.9	46.1	23.9	15.6	17.5	13.5

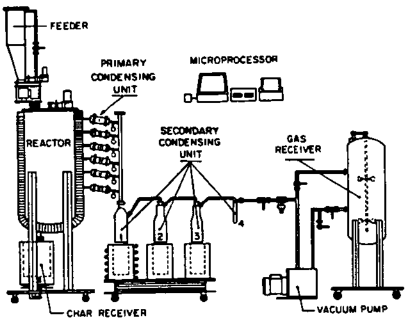

Fig. 1 - Scheme of the vacuum pyrolysis process development unit.

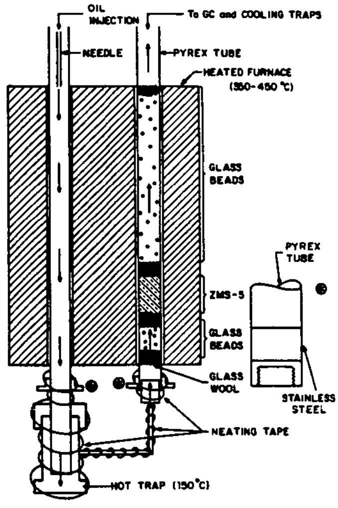

Fig. 2 - Scheme of the oil pretreatment device and reactor.

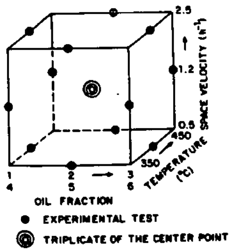

Fig. 3 - Box Behnken Experimental Design

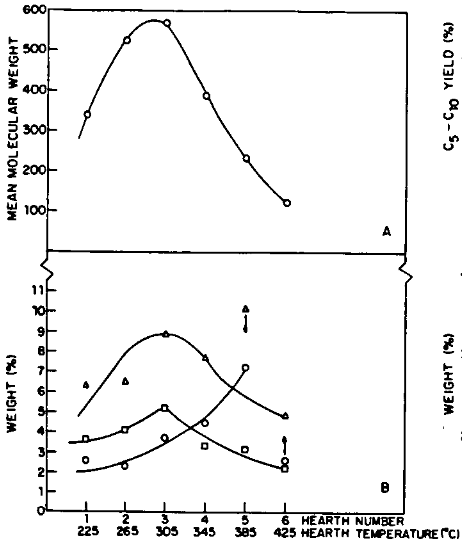

Fig. 4 - Characteristics of the pyrolytic oils. A - average molecular weight. B - Wt % of acetic acid (□), formic acid (o) and sum of acetic + formic acids (Δ).

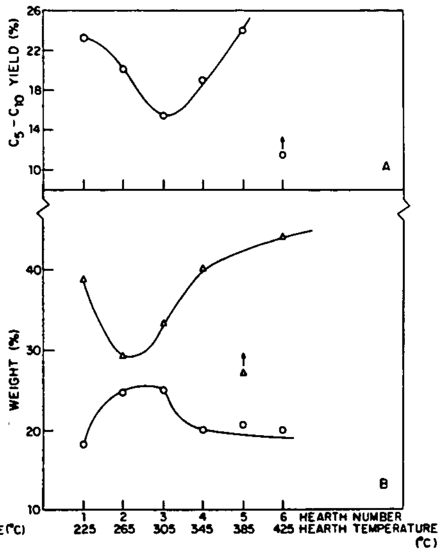

Fig. 5 - Average values for C_5-C_{10} yields (A) and coke (B o) and residuum (B Δ).

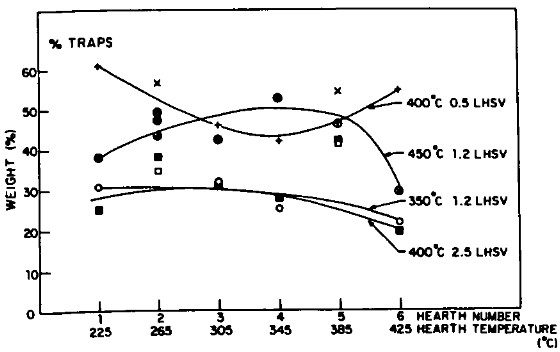

Fig. 6 - Weight % of the products collected in the traps.

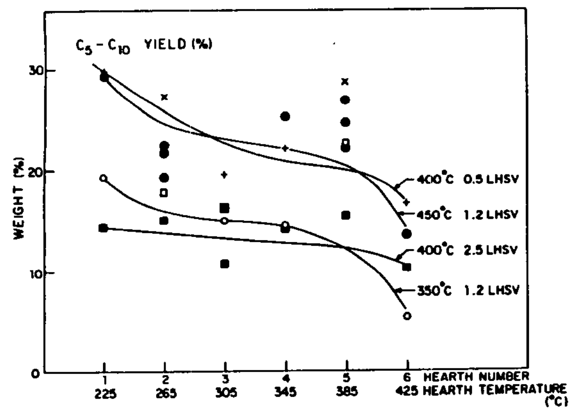

Fig. 7 - C_5-C_{10} yields

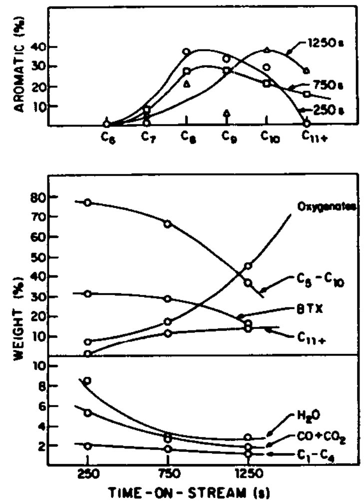

Fig. 9 - Product distribution as a function of time-on-stream

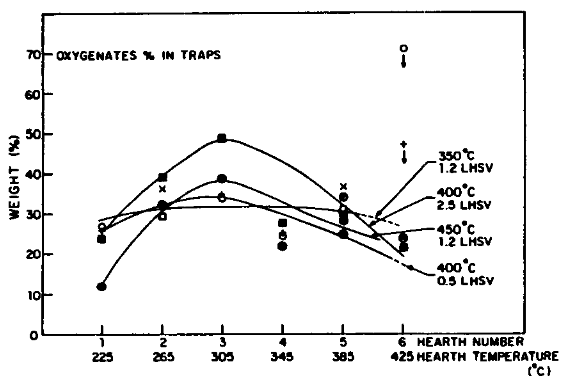

Fig. 8 - Weight % of oxygenates in the traps.